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**AN APPARATUS FOR THE MEASURE-
MENT OF THE PARTIAL VAPOR
PRESSURES OF THE BINARY
SYSTEM AMMONIA--WATER**

BY

ARNOLD O. BECKMAN

THESIS

FOR THE

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Arnold Orville Beckman

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IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science

Richard Dietrichson

Instructor in Charge

APPROVED:

D. W. Parr

acting

HEAD OF DEPARTMENT OF

Chemistry

517321



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I. Introduction.

The measurement of the total and partial vapor pressures of aqueous ammonia solutions was undertaken primarily for the purpose of obtaining new data for use in connection with the absorption system of ammonia refrigeration. In developing the thermodynamic relations of the properties of ammonia solutions to be used in this work, it was found that the data available was neither sufficiently accurate nor extensive enough in its scope to permit of satisfactory mathematical treatment. There was an urgent need for accurate determinations of the vapor pressures of ammonia solutions whose concentrations ranged from 0 to 50 percent at temperatures of 0° to 120°C.

From a theoretical standpoint the determination of the partial pressures should prove very interesting. The anomalous behaviors of both water and ammonia are demonstrated in many of their properties and it is reasonable to expect a similar non-conformity with the laws governing vapor pressure. From accurate measurements of the partial pressures, the deviation from Raoult's and Henry's laws could be expressed. Since the determination of the partial pressures involves a measurement of the total vapor pressures, it was decided to carry out both determinations.

The problem undertaken, then, was one of designing an apparatus which would permit the determination with a high degree of accuracy of the total and partial vapor pressures of aqueous ammonia solutions of all concentrations over a

temperature range of 0° to 120° C. and a pressure range of approximately 15 to 800 cm. of Hg ($1/5$ to 10 atmos.), these limits being those met with in actual refrigerating practise and sufficient in extent for the theoretical considerations.

II. Historical.

The first determinations of the vapor pressures of aqueous ammonia solutions which were of any importance were those obtained by Sims¹ in 1861. He determined the total vapor pressures by the static method at the temperatures of 0°, 20°, 40°, and 100°C. He employed only very dilute solutions in his work.

Perman^{2,3,4}, in 1903, was the first to make measurements over any considerable range of concentrations, working with solutions containing 0 to 22.5 percent of ammonia at temperatures of 0° to 60°C., no pressures higher than 535 mm. of Hg being measured, however. He used a dynamic method which consisted of blowing air through ammonia solutions under certain conditions, then from the composition of the resulting vapor calculating the partial vapor pressures of its constituents. This method is not applicable to high concentrations, however, because the ratio of the ammonia content to that of the water in the vapor drawn off becomes so great that the results are inaccurate. Even at the concentrations used by Perman the results did not check very well. Perman's work, also, is based upon several assumptions of rather doubtful validity (as the statement that Raoult's law holds for ammonia solutions) that his results, while seeming to check fairly well with themselves, must, nevertheless, be looked upon with suspicion.

The most recent, and to this date, the most reliable data is that secured by Hilde Mollier⁵ in 1908, working in the laboratories at München. Her report included values of vapor press-

ures up to 700 cm. of Hg (9.2 atmos.), at temperatures of 0° to 120° C., and concentrations of 11.80, 23.39, 33.73, 41.55, and 50.31 percent. The method followed was the usual static method in which the pressure above the ammonia solution contained in a closed vessel surrounded by a constant-temperature bath was measured by an open manometer. From the data given in her report however, it is seen that the analyses of the ammonia solutions do not check within the desired degree of accuracy. Moreover, her work affords only the total vapor pressures.

III. Theoretical.

The usual method of obtaining the partial vapor pressures of any substance in solution is to assume that Raoult's law holds and then to calculate the partial vapor pressures from the total vapor pressures and the compositions of the solutions. In this case, however, since it is desired to show whether or not Raoult's law does hold for aqueous ammonia solutions, the law cannot be used in the calculations. Since, then, the partial vapor pressures cannot be calculated from a knowledge of the composition of the liquid phase, some method must be devised whereby the vapor phase may be analyzed. Then, knowing the composition of the vapor, the total vapor pressure, and the vapor pressure of water (from Landolt-Börnstein), the application of Dalton's law will give the partial vapor pressure of the ammonia.

In order to make possible an accurate analysis of the vapor phase, it is desirable to have a large quantity of the vapor for analysis. Consequently, the apparatus should be designed with a comparatively large space for the vapor phase.

Since samples of both the vapor phase and the liquid phase are to be removed for analysis, some arrangement should be incorporated whereby the composition of each phase will not change while the portion of the other phase is being removed. This could be done by separating the two phases after equilibrium has obtained and the total vapor pressure determined.

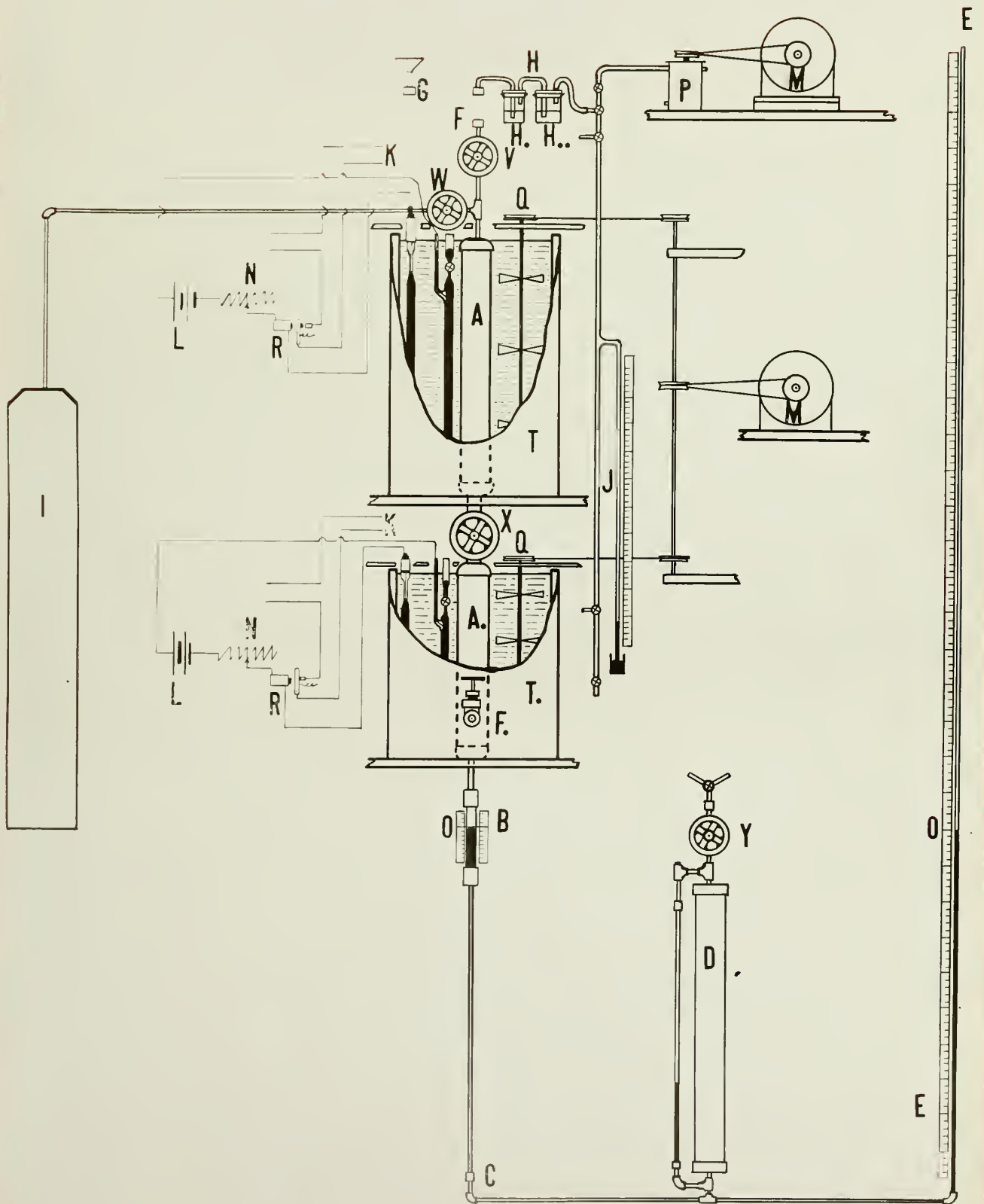
In order to permit the use of highly concentrated solutions with their accompanying high vapor pressures, it seems advisable to prepare the solutions within the apparatus itself. As

commercial ammonia can be obtained with a high degree of purity, it could be used for this purpose. As ordinarily sold in tanks it is under a pressure of approximately 10 atmospheres at room temperature, so that the ammonia could be forced by its own pressure into the apparatus.

For measuring the pressures, the mercury manometer offers itself as the best device. It would be extremely difficult to find pressure gauges made of a material not readily attacked by ammonia, and even if such a device were available, it would need frequent calibration. The mercury manometer is simple in operation and gives the absolute values directly.

The apparatus must be made of some substance not readily attacked by either ammonia or mercury. The two materials which suggested themselves were glass and iron. A test was made in which pieces of glass and iron were boiled for the same length of time in ammonia solution. It was found that the glass specimen lost much more in weight than did the iron specimen. For this reason the apparatus was made of iron. Iron has the additional advantage, also, of possessing a much higher tensile strength so that the higher pressures could be used with safety in the apparatus.

With the foregoing considerations in mind, the apparatus described in the following pages was designed and constructed.



IV. The Apparatus.

The ammonia solution is contained in the vessels A and A., made of 2 inch black wrought-iron pipe. The upper container A is 22 inches long and has a capacity of 942 cc. The lower container A. is 16 inches long with a capacity of 650 cc. In order to facilitate the attainment of equilibrium within the system, A. is provided with a baffle-plate arrangement made by twisting an iron rod of small diameter into a loose, irregular bundle. The two pipes are closed by caps at each end, the two adjoining ends being connected through the 1 inch valve X. Into the cap at the bottom of A. is screwed an 1/8 inch pipe which extends over to the mercury reservoir and manometer. In assembling the apparatus it was found necessary to put a thin mixture of glycerine-litharge cement on the pipe threads at all of the joints for only in this manner could a vacuum-tight joint be obtained.

Since it is necessary to have some method of keeping the meniscus of the mercury column within the apparatus at a constant level, some device had to be installed for this purpose. A glass tube was inserted at B so that the meniscus could be easily seen and kept at a certain mark. A great deal of difficulty was experienced in finding a suitable means of sealing the glass tube to the iron pipe so that the joint would be impervious to ammonia and mercury, and at the same time, be vacuum-tight. The method which was finally successful was this:

The 1/8 inch pipe on either side of the glass tube was

fitted with a $3/8$ inch bushing on which was screwed a $3/8$ inch coupling. The glass tube was then selected of such a size that it fitted easily into the couplings. The space between the glass tube and the couplings was filled with glycerine-litharge cement. After the cement had hardened, it was covered with a layer of deKhotinsky cement. This last covering of the deKhotinsky cement was found to be necessary as the glycerine-litharge cement is slightly porous and allowed air to diffuse slowly into the vessels A and A. when the apparatus was evacuated. The layer of deKhotinsky cement remedied this trouble entirely.

C is a black-iron union inserted for the purpose of simplifying the assembling of the apparatus. It is located about 80 cm. below the meniscus line at B so that at all times there is pressure within the union. This was found necessary as the union leaked slightly under high vacuum. Under pressure, however, the union did not leak, the mercury inside evidently providing a sufficient seal.

D is a reservoir for the mercury made of 2 inch iron pipe. A gauge-tube at the side registers the level of the mercury within the tube. At the top of the tube a needle-valve Y is placed. On top of Y is a two-way stopcock. One side of the stopcock is connected to the compressed-air line and the other to the vacuum line in the laboratory. Then, by turning the glass stopcock, either pressure or vacuum is put upon the valve Y. Since Y is a needle-valve, this pressure or vacuum can be very gradually applied to the mercury within the tube, thus allowing a very accurate adjustment of the meniscus level. A

plug in the tee at the bottom of the guage-tube affords a means of filling the tube with mercury and a similar plug at the bottom permits the tube to be emptied.

The manometer E is simply a straight glass tube inserted into a coupling and sealed as in the case of the glass tube at B. In this case, however, the tube is sealed in with deKhotinsky cement alone as the ammonia does not come in contact with this part of the apparatus. There is the added advantage, too, that the manometer tube can be removed at any time by simply heating the joint. This is helpful when the open manometer is replaced by a closed manometer for use at higher pressures. The height of the meniscus may be read from the scale shown or by means of a cathetometer.

Into the vessel A. a $\frac{1}{2}$ inch pipe is soldered which terminates in the valve F on the outside of the thermostat tank. This valve is for the purpose of withdrawing the sample of the liquid phase from A. as will be explained later. At the top of A, pipe connections are so arranged that by means of the valve W ammonia gas from the tank I may be introduced. The valve V has several functions. It allows the vessels A and A. to be evacuated by connecting the vacuum line with the system through the connection at F. By connecting through the collecting vessels H a sample of the vapor may be brought off for analysis. By connecting with G water may be introduced for the purpose of making the ammonia solutions.

For making these connections, Y is connected to the part of a union containing the female thread. Then parts of exactly similar unions containing the male thread are attached to G,H,

etc., so that connection may be made with any one by screwing the union together. G is a glass funnel sealed into the union with deKhotinsky cement. H consists of two collecting flasks, H. containing standard dilute sulfuric acid and H.. containing concentrated sulfuric acid. The latter vessel is connected through a glass stopcock to the vacuum line J.

The vacuum line J is made of $1/8$ inch pipe with glass stopcocks sealed in as shown in the diagram. The stopcocks are sealed in with deKhotinsky cement in a manner similar to that of sealing in the manometer tube. The upper stopcock is for the purpose of shutting the vacuum pump P from the line. The next stopcock allows the vacuum to be applied to the sampling vessels. The third stopcock, when connected to F by means of pressure tubing, allows the two vessels A and A. to be evacuated. At the bottom of J another stopcock is placed to be used in drawing off the samples of the liquid phase. Immediately above this another stopcock is placed so that the vacuum within the line may be released at any time. The manometer J registers the degree of vacuum within the line.

The vessels A and A. are surrounded by the thermostat tanks T and T.. The thermostat tanks are made of sheet iron surrounded by a thick layer of wool to insulate the tanks from the surrounding atmosphere. The stirrers Q, operated from the line shaft by the motor M, are of sufficient size to give adequate stirring. The temperature is regulated by the U-shaped mercury regulators shown. These operate in the usual way, the low-voltage current being furnished by the dry cells L. The resistance N regulates the current which flows through the

relay R. On the other side of the relay, the 110 volt current is connected through the relay to the heating lamps at K.

In addition to this regulation, there are coils (not shown in the diagram) within the tank through which cold water may be circulated. The liquid in the tanks is water for the measurements at 0 C. and oil for the other temperatures.

The valves V, W, F., and Y are made especially for use with ammonia solutions. They are built by York and Company, and are of the so-called expansion type. The needle seats both when the valve is open and when it is closed. This eliminates the leaking around the valve stem which would otherwise occur, and permits a high degree of vacuum, or a high pressure, to be maintained indefinitely. Since the valves are of the needle type, they permit a very gradual release of the pressure. The valve X is of the globe type and also seats either open or closed.

V. Calibration.

In using the apparatus, the first thing to be carried out is the calibration of the manometer. A mark O is drawn upon the scale at B as the fixed position of the meniscus. Then, with the vessels A and A. open to the atmosphere, the level O should be marked upon the manometer scale. Then, in taking readings, the position of the manometer meniscus above or below that mark will be a measure of pressure above or below atmospheric which exists within the apparatus.

The pressure which is wanted is that at the surface of the liquid phase. Therefore the pressure read upon the manometer must be corrected for the pressure due to the liquid within A.

$$P_v = P_t - P_l$$

where

P_v = the vapor pressure of the solution.

P_t = the total pressure as read upon the manometer.

P_l = the pressure due to the column of liquid.

P_t can be read directly from the manometer; P_v is the quantity to be determined experimentally; P_l must be calculated.

The pressure at the bottom of the column of ammonia solution is equal to the weight of the solution divided by the cross-section area of the tube. The area of the cross-section of the 2 inch pipe of the vessel A. may be found by adding a known volume of water to the vessel and measuring the height

of the resulting column of liquid. (This must, of course, be done before the apparatus is assembled.)

Then

$$\frac{V}{H} = A.$$

where

V = volume of the water added.

H = height of resulting column of water.

A = cross-section area of the pipe.

The calculation of the weight of the solution is simplified if it is considered as being made up of two parts: ammonia, whose weight is a variable quantity depending upon the concentration of the solution, and water, which has a constant weight in all determinations. This last statement is true providing the solutions are made by adding ammonia to the same weight of water in each determination, and that is the method of procedure which will be followed in using the apparatus. The pressure due to the water then, is a constant correction.

$$\frac{W_{H_2O}}{A} = P_{H_2O}$$

When

W_{H_2O} = weight of the water added (500 grams).

A = cross-section area of the tube.

P_{H_2O} = pressure due to the water in the solution.
(grams-weight).

There remains the problem of finding the pressure due to the ammonia in the solution.

From the analysis of the liquid phase, the weight of the ammonia in the solution may be found.

Then

$$\frac{W_{\text{NH}_3}}{A} = P_{\text{NH}_3}$$

This quantity must be determined for each experiment.

It will be noticed that the pressure due to the solution was calculated on the assumption that all of the solution was in A., a tube of constant cross-section area. There is an additional pressure due to the liquid contained in the 1/8 inch pipe and the glass tube leading from A. to the mercury meniscus at B. The volume of this amount of the solution is so small that it need not be subtracted from the original 500 cc. of the water, (all of which was assumed to be in A.) on account of the large cross-section area of A.. In the 1/8 inch pipe and the glass tube, however, the cross-section area is so small that the resulting height of this small volume must be considered. This additional pressure may be found by measuring the distance from the meniscus level at O to the vessel A. This height, multiplied by the density of the solution (from Landolt-Börnstein) for the particular concentration will give the last correction to be made.

$$H \cdot D = P_x$$

where

H = the height from O to A.

D = the density of the solution.

P_x = pressure correction for this height of solution.

Then

$$P_1 = \frac{P_{H_2O} + P_{NH_3} + P_x}{13.595}$$

where

P_1 = the pressure due to the total weight of the solution.
(in cm. of Hg.)

VI. Operation.

For the 0° C. readings fill the tanks with crushed ice. For the higher temperatures fill the tanks with oil. Set the thermostat regulators to give the desired temperatures.

Open X, connect F to the vacuum line J and evacuate A and A.. Close V, attach G and add 500 cc. of water, closing V quickly as soon as all of the water is introduced into A to prevent the introduction of much air.

Open W, admitting the ammonia gas until the solution is of the desired strength. This can be told roughly from the reading of the manometer. Stir the mixture somewhat by lowering and raising the mercury in A.. Close X and evacuate A. Open X for a minute and evacuate A again. This process eliminates any air which may be contained within the system. Close V and stir until equilibrium is obtained. This can be judged from the readings of the manometer. When there is no difference between successive readings taken a few minutes apart, the system is in equilibrium.

While the system is coming to equilibrium, H (and a similar collecting device for the liquid phase) should be weighed. After the equilibrium has been obtained, read the manometer E, close X and draw off a sample of the vapor phase through H. and H.. . Draw off a sample of the liquid phase through F.. In drawing off the sample be sure to get the pressure on the outer end of the sampling train lower than that within the system, otherwise the sulfuric acid will be drawn

into the apparatus. For the low concentrations and temperatures it will be necessary to connect the collecting vessels to the vacuum line J, but at the higher concentrations and temperatures the pressure within the apparatus will be higher than atmospheric so that this procedure will not be necessary.

Weigh the sampling trains again, then titrate the excess acid with N/10 NaOH. This will give the weight of the ammonia in the vapor and liquid phases. The weight of the water in each case is found by subtracting the weight of the ammonia from the total increase in weight of the collecting vessels.

The weight of the ammonia is then used to determine the pressure corrections as described under Calibration.

The treatment of the results is beyond the scope of this paper. Work is in progress on the actual measurement of the total and partial vapor pressures and the data obtained will be submitted at a later date.

VII. Summary.

1. An apparatus has been designed and constructed which will permit measurements to be made with a high degree of accuracy of the total and partial vapor pressures of aqueous ammonia solutions.
2. The calibration and the mode of operation have been described in detail.
3. Work is in progress on the measurement of the total and partial vapor pressures of aqueous ammonia solutions.

VIII. Acknowledgments.

The apparatus described in this paper was designed and constructed by the joint efforts of Mr. Thomas A. Wilson and the author.

The author wishes to express his sincere gratitude to those who have helped him in his work on this problem. Dr. G. Dietrichson, under whose direction the work was carried out, has maintained an untiring interest in the problem and has given many thoughtful criticisms and suggestions. Dr. W.H. Rodebush and T.E. Phipps have offered much valuable advice which greatly simplified the construction of the apparatus.

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